Growth Optimization and Annealing of Mercury Based Cuprate Superconductors

$HgBa_2CuO_{4+\delta}$ and $HgBa_2CaCu_2O_{6+\delta}$

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Abstract: The phenomenon of high-temperature superconductivity in the mercury-based cuprates $HgBa_2CuO_{4+\delta}$ and $HgBa_2CaCu_2O_{6+\delta}$ is investigated. Additionally, the growth and characterization of samples is discussed. It is shown that the doping of $HgBa_2CuO_{4+\delta}$ samples can be controlled by annealing them under certain conditions to generate samples with different doping levels and superconducting transition temperatures. Finally, the effect of using different amounts of HgO during growths of $HgBa_2CaCu_2O_{6+\delta}$ is discussed and it is shown that using more HgO leads to samples with higher transition temperatures but broader superconducting transitions.

Introduction

Since the discovery of superconductivity in mercury in 1911, superconductors have been an active area of physics research. Superconductors are materials that, at sufficiently low temperatures, exhibit zero electrical resistance and expel all internal magnetic fields in a property known as the Meissner effect. In 1957, superconductivity was given a theoretical explanation by Bardeen, Cooper, and Schrieffer with their namesake theory that electrons in superconducting materials form Cooper pairs below the superconducting transition temperature, or T_c, of the material [1].

However, in 1986, a new class of superconductors was discovered that exhibit superconductivity at much higher temperatures than originally predicted under BCS theory. These compounds, known as the cuprates, are ceramic materials characterized by simple lattice structures featuring layers of copper and oxygen atoms. Today, a wide variety of cuprates have been created with T_c as high as 135 K at ambient pressure and 163 K under hydrostatic pressure, but there still exists no explanation for the mechanism behind superconductivity in the cuprates.

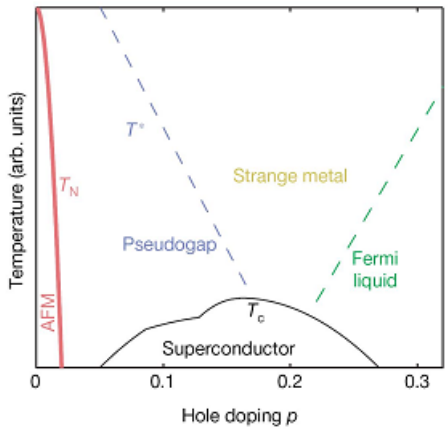


Figure 1 [2] – The phase diagram for a cuprate superconductor based on the temperature and hole doping level of the sample. The black dome represents the superconducting phase. The phases above have many anomalous physical properties and are not yet well understood.

In addition, the cuprates exhibit a variety of interesting and unexpected states depending on both their temperature and doping (Figure 1). This includes the so-called pseudogap phase, in which an energy gap causes unexpected physical properties. Finding the mechanism and better understanding the properties of the intermediate phases remains an important problem in condensed matter physics today.

The Mercury-Based Cuprates

The mercury-based cuprates are the series of compounds with the chemical formulas $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$. They are ideal for study because they exhibit the highest T_c of any known cuprate

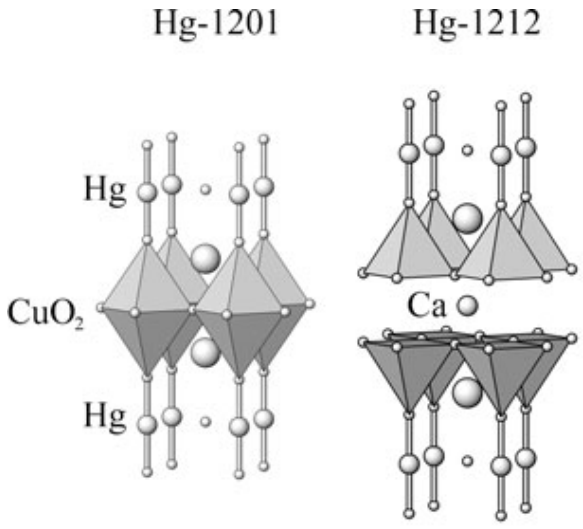


Figure 2 [4] – The lattice structures of Hg1201 and Hg1212. The latter compound features intermediate calcium atoms as well as doubled copper-oxygen layers.

superconductors [3] and because of their simple tetragonal lattice structures (Figure 2). The first two compounds in the series, $HgBa_2CuO_{4+\delta}$ (or Hg1201) and $HgBa_2CaCu_2O_{6+\delta}$ (or Hg1212), are most commonly studied because it is possible to produce relatively high quality single crystal samples of each compound.

The growth process for Hg1201 has been optimized to reliably produce quality crystals, and has been previously described in detail [5]. The growth of Hg1212 samples follows a similar process, but much work is still ongoing to try to optimize this process. Like for Hg1201, a Ba_2CuO_3 precursor is first formed by sintering $Ba(NO_3)_2$ and CuO powders. The powders are ground together in a mortar and pestle and then heated for 17 hours while being exposed to a flow of pure oxygen, removing water and other waste compounds that could lead to impurities in the samples.

Next, 2.58 g of the precursor is combined with 0.34 g of CaO powder and ground thoroughly in a mortar and pestle. This mixture is put into a zirconium crucible with 1.9 g of HgO and sealed inside a quartz tube. In addition, 20 mg of $MgSO_4$ hydrate is added to the quartz tube in order to provide water, which is important to the crystallization process. For Hg1201, there has been evidence to show that increasing the amount of $MgSO_4$ used increases the size of crystals grown, but also causes a drop in the quality of the crystals. The amounts of HgO and $MgSO_4$ used in particular are still being adjusted, and the effects of these adjustments will be discussed.

Then, the quartz tube is heated under the following temperature profile. First, it is heated to 780°C and held there for 20 hours. This allows the HgO to decompose and react with the precursor to form Hg1212 in the crucible. Next, it is heated slowly to 1020°C and held there for 3 hours to allow the Hg1212 to melt and mix together. Then, it is cooled first to 900°C to allow

crystallization and then to room temperature so that the quartz tube can be safely handled. This is similar to the growth profile used for single layer Hg1201, but the exact process for the formation of Hg1212 is not yet fully understood.

Finally, the quartz tube and crucible are broken using a hammer to reveal a cone at the bottom of the crucible containing Hg1212 and unwanted side products. Unlike for Hg1201, the cone is broken immediately and can then be picked through to find the generated Hg1212 crystals.

Sample Characterization

Grown crystals of Hg1201 and Hg1212 can be characterized using a Magnetic Properties Measurement System (MPMS), which measures the magnetization of the sample in order to find its T_c. In addition to finding the T_c of the sample, the quality of the sample can be determined in a couple of ways. For Hg1201, magnetization measurements are made twice, once when the sample is cooled in a small magnetic field (field-cooled, FC), and again with no field (zero-field-cooled, ZFC). Taking the ratio of the FC to ZFC response at low temperatures gives an estimate

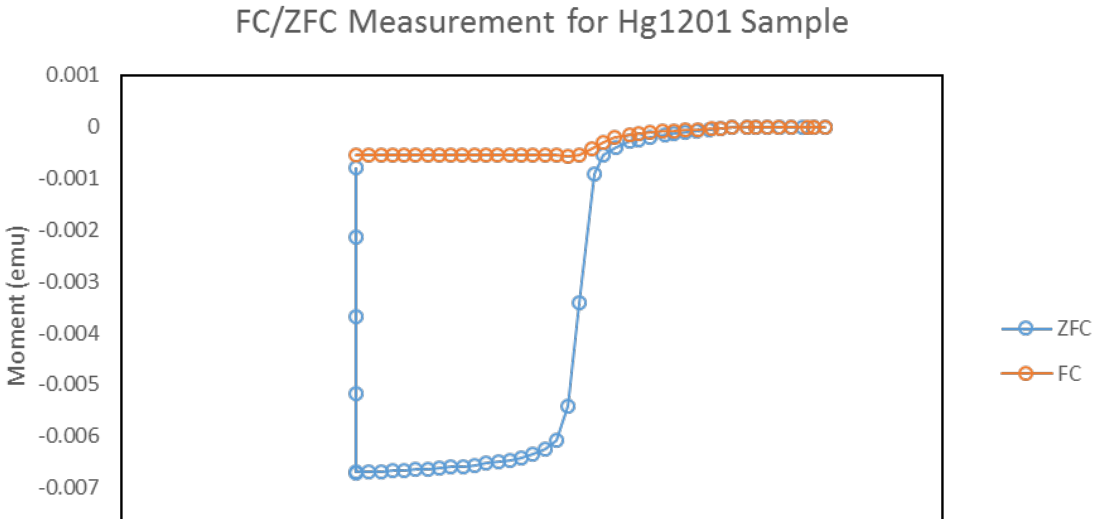
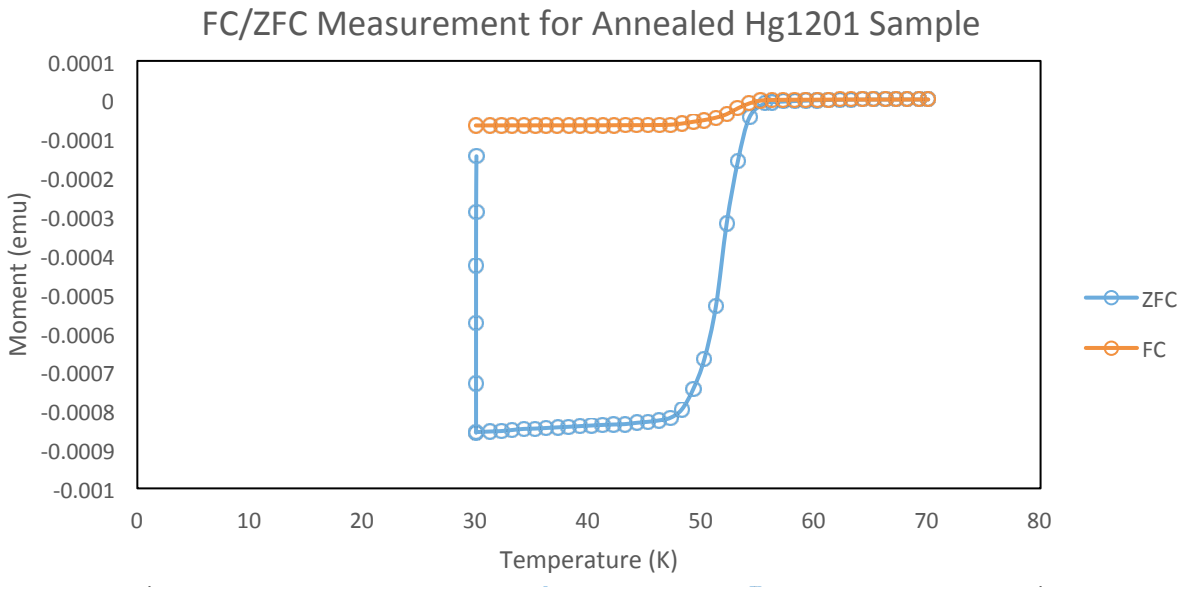


Figure 3 – MPMS measurements for an as-grown sample of Hg1201. The sharp change in magnetic moment represents the transition between superconducting and non-superconducting states. The T_c of this sample is around 80 K. First, the sample is cooled under a magnetic field (FC; upper data points), then again with no magnetic field (ZFC; lower data points). The FC/ZFC ratio of this sample is about 10%, which indicates that the sample is of relatively low quality.

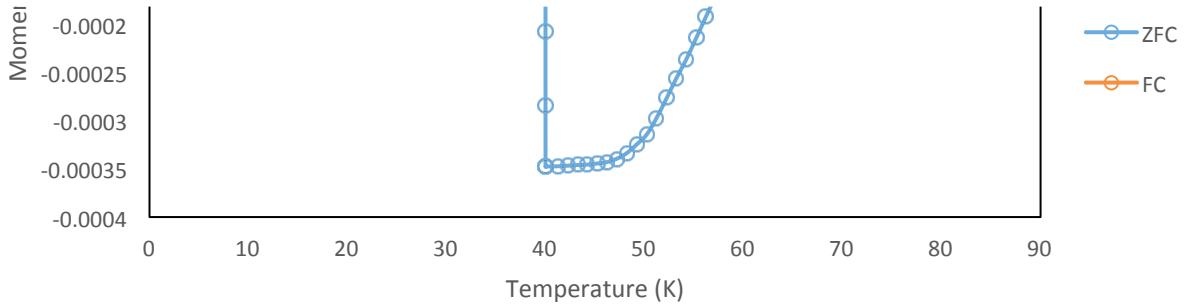
of the sample quality for Hg1201 crystals. In addition, the MPMS measures the magnetic response denoting the transition to a superconducting state over a range of temperatures, with the T_c being defined as the midpoint of this transition. The width of the transition is another good indicator of sample quality, with a steeper transition denoting a higher sample quality. Figure 3 shows an MPMS measurement performed on an as-grown crystal of Hg1201.

Doping Control

Once samples of Hg1201 and Hg1212 have been created, they can be used for a variety of measurements and tests. One common procedure is to anneal the crystals under different conditions in order to try to control their doping level. By changing the hole concentration of the CuO planes in the crystals, different parts of the phase diagram can be reached and their properties can be examined. Crystals can be annealed in different gases or a vacuum, at different temperatures, at different pressures, or for different amounts of time in order to generate a wide variety of doping levels for other tests. These samples can then be used again for characterization or other types of measurements.



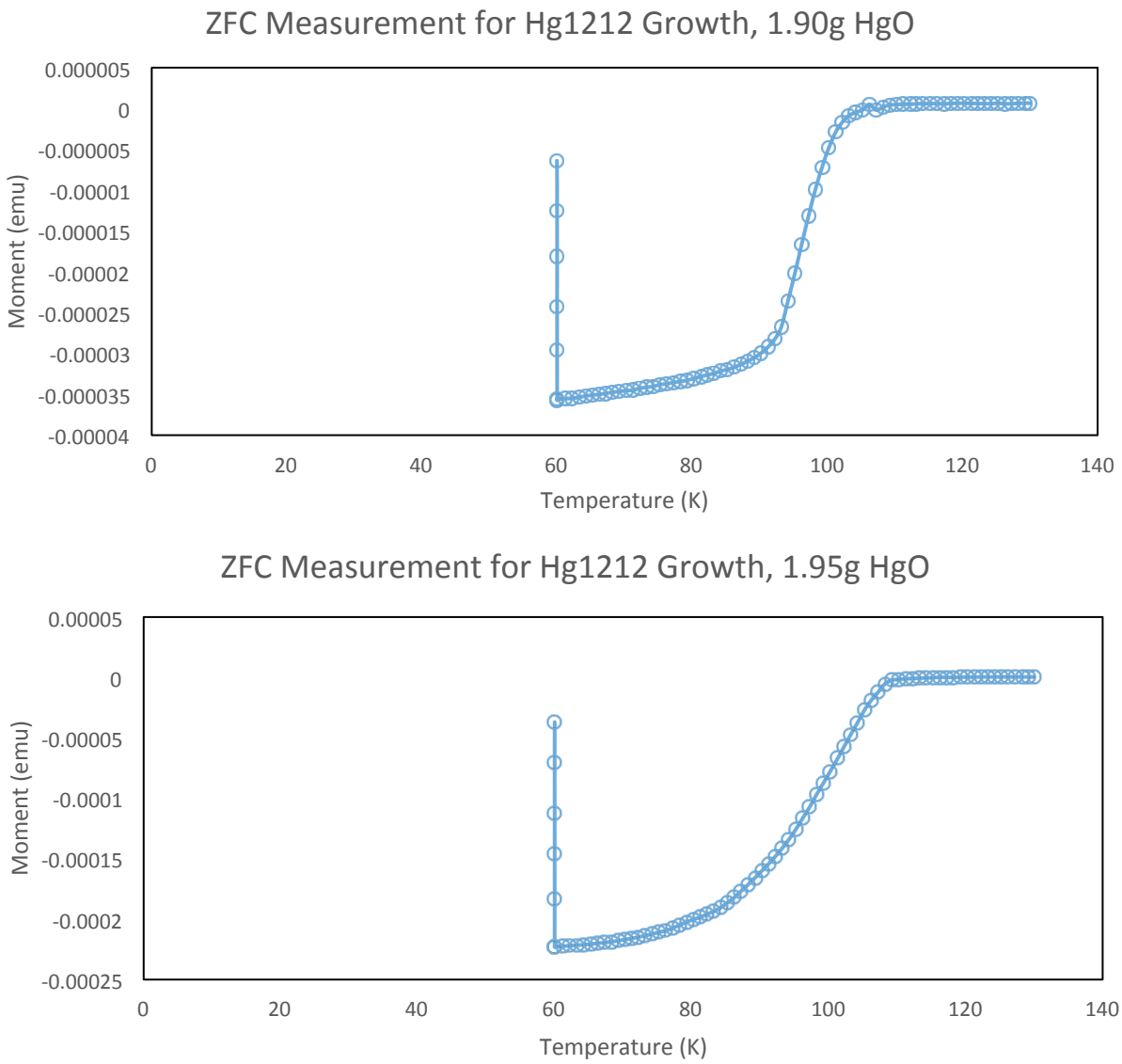
Figures 4,5 – MPMS measurements for two Hg1201 samples annealed at 550°C and 1.7 mtorr for 2 weeks. The T_c for both samples lies above the targeted T_c of 45K.



Figures 4 and 5 show the results of two vacuum anneals performed on single layer Hg1201 samples. The samples were kept under a 1.7 mtorr vacuum in a furnace set to 550°C for 2 weeks. The target T_c for these anneals were 45K. The actual T_c for the samples after annealing were 58K and 53K respectively. This shows that we were successful in creating underdoped samples, but refining the annealing conditions necessary to generate samples with more precise T_c and doping levels is a subject of continuing research.

Hg1212 Growth Optimization

In an effort to better optimize the growth process for Hg1212, the effect of changing the amount of HgO used for growths has recently been studied. Two growths were performed side by side, keeping everything the same except for using the normal 1.90g HgO for the first growth and increasing this to 1.95g HgO for the second growth. It was seen that even this small change had a very large impact on the crystals generated, both in terms of T_c and sample quality, as is shown in figures 6 and 7. The cause for this phenomenon is not yet known and the process of optimizing the Hg1212 growth process to reliably create large, high-quality samples remains ongoing.



Figures 6,7 – MPMS measurements for two Hg1212 samples grown using different amounts of HgO. The growth with a larger amount of HgO used had a T_c about 5K higher, but a much broader transition between superconducting and non-superconducting states.

Future Study

While much progress has been made, there is still a long ways to go to understand the phenomenon of high-temperature superconductivity in the cuprates. More growths and anneals of Hg1201 and Hg1212 must be performed and these processes must be further optimized in

order to get a wide range of quality samples to probe the entire cuprate phase diagram. Once better samples are obtained, various transport measurements must be performed that can give insight into certain properties of the samples that cannot be found solely from characterization measurements. Transport measurements such as Hall Effect and Thermoelectric Power have been performed on Hg1201 samples in the past, but these measurements still have much to teach us and must be performed on samples of Hg1212 as well in order to continue the search for the cause of high-temperature superconductivity in the cuprates.

References

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